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Thermoluminescence of Cu doped ZnS nanoparticles

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Abstract

ZnS nanoparticles doped with Cu were synthesized by wet chemical route method at 4°C temperature. We have investigated the Thermoluminescence (TL) properties of the undoped ZnS and Cu doped ZnS with increase in Cu concentration from 0.5 millimole to 1.5 millimole and also study for different weight of Sodium Hexa Meta Phosphate (SHMP) capping agent from 2gm to 10gm. The XRD studies indicate that most of the samples are cubic in nature. The broadening of peaks tends to increase with increasing weight of capping agent showing decrease in particle size. The crystalline size computed using Scherer formula is found 2nm to 3nm. Absorption spectra show blue shift with different weight of capping agent. TL glow curve shows a single peak at 543 K temperature. Variation in TL intensity as a function of copper concentration is studied and 1mM is found to be the optimum concentration for TL. The trap parameters namely, activation energy (E), order of kinetics (b) and frequency factor(s) of ZnS: Cu sample have been determined using Chen's method. The effect of heating rates and UV radiation dose for different time on TL glow curve has also been studied.

Keywords: ZnS:Cu, Thermoluminescence, Photoluminescence, Absorption spectra, Nanophosphor, XRD And UV

INTRODUCTION

Thermoluminescence is the emission of light from a solid either inorganic, semiconductor or an insulator when it is heated after its exposure to some radiation.

Thermoluminescence is one of the long investigated fields. Various aspects of TL have been theoretically as well as experimentally studied till date. The thermoluminescence method is generally used to study defects in insulators and materials. Moreover, this method is successfully applied in the field of radiation dosimetry [1]. Research on nanosized II -VI semiconductors stimulated great interest in recent years and showed great potential applications because of their unique properties [2-4], such as unusual luminescent properties induced by quantum-size effect [5]. Efforts were also made in realizing luminescence-tunable materials simply by changing the particle size with narrow size distribution [6] and progress in this regard indicated that nanosized semiconductor particles can be used as luminescent materials. Doped nanosized semiconductors, ZnS: Mn, new kind of luminescent materials, make the research more vigorous [7-9] and the rich field of doped semiconductor needs further exploration. By taking the advantage of developments of in preparation, not only the transition metal ions [10-12]. But also the rare earth ions [13] are managed to be doped into proper hosts in the nonosized range. Doping of ZnS nanoparticles by transition metal ions e.g. Mn^{2+} [14, 15] ,Cu^{2+} [16,17] and rare earth ions e.g. Eu^{2+} [18,19] have been successfully done by techniques such as thermal evaporation, sol-gel processing, co-precipitation, microemulsions and wet chemical method etc. These doped ZnS semiconductor material have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, and optical sensors. Accordingly, study of luminescence properties of ZnS has received special attention. In addition to the blue luminescence of ZnS host, emission in different visible bands related to the various dopants has been reported. This includes orange luminescence in ZnS: Mn nanoparticles, attributed to the $^4T1$-$^6A_1$ transition of Mn^{2+} ions excited via energy transfer from the host ZnS, red emission from the characteristics $4f^7$ - $4f^65d^1$ transition of Eu^{2+} in ZnS:Eu nanoparticles and green luminescence in ZnS: Cu nanoparticles may be associated to the 3d level transitions of Cu^{2+} [20- 21].

EXPERIMENTAL

In principle, the preparation method adopted here is wet chemical route method. Different weight (2gm,4gm. 6gm,10gm) of sodium hexa meta phosphate (SHMP) (sigma aidrich AR grade) was separately dissolved in de-ionized water and stirred. To each of this an aqueous solution of 0.25M Zn $(CH_3COO)_2$ and 1mM $Cu(CH_3COO)_2$ was mixed together and stirred constantly and heated till boiling. After cooling to room temperature, 0.25 M sodium sulphide was added drop wise in an ice bath with constant stirring, resulting in formation of ZnS: Cu nanoparticles almost immediately. The supernatant was then centrifuged to separate undesired agglomerates. After washing the particles with de-ionized water, the samples were dried to obtain fine powder of ZnS: Cu nanoparticles. The samples were prepared by using different preparation conditions and characterized by XRD –Burker D8 advances X-ray Diffractometer at IUC Indore, UV-VIS spectroscopy Perkins-Elmer Model Lambda 950 Spectrophotometer, TL – TLD Reader TL 1009 Nucleonix.

RESULTS AND DISCUSSION

Fig.(1) Shows the XRD patterns for ZnS: Cu nanophosphors. From XRD patterns three diffraction peaks were observed at 28.77°, 49.11° and 57.33°.. This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes, respectively [22]. The average size of doped nanoparticles, estimated from the Debye –Scherrer formula, was about 2nm to3 nm.

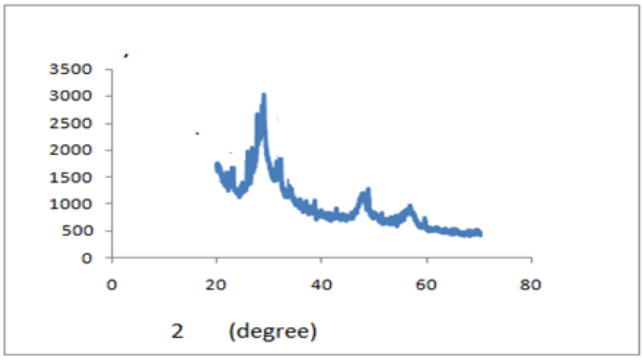

Fig 1. XRD scan of doped ZnS nanoparticle.

Fig. (2) Shows the absorption spectra of ZnS: Cu nanophosphors for different weight of SHMP capping agent. It is seen that the absorption edge shifts towards shorter wavelength side with increasing weight of capping agent and the effective band gap varies from 3.88eV to 5.28eV.

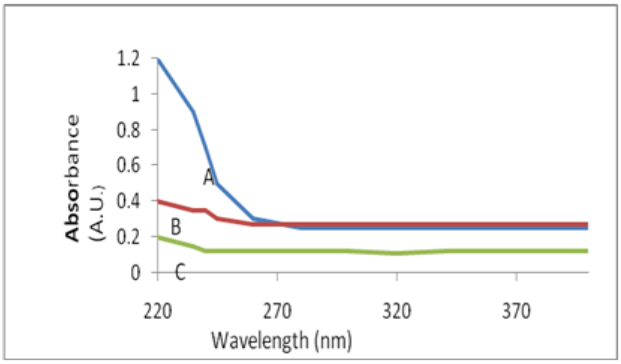

Fig 2. Absorption spectra of ZnS: Cu nanoparticles synthesized with different weight of SHMP. A-2gmSHMP, B-4gmSHMP C-6gmSHMP.

Fig. (3) Shows the TL glow curve of ZnS: Cu for different concentration of copper at 5minute UV radiation time. In the present case the TL intensity increases with coper concentration up to 1mM and afterwards it decreases. If the concentration of impurities increases from a particular amount, they may act as self quencher by non-radiative transitions resulting in fall in the intensity of the luminescence. The fall in TL intensity may be attributed to the well known concentration quenching effect of dopant. Hence the optimum impurity concentration of Cu in ZnS 5min. UV exposure is 1mM since at higher concentrations the TL intensity falls.

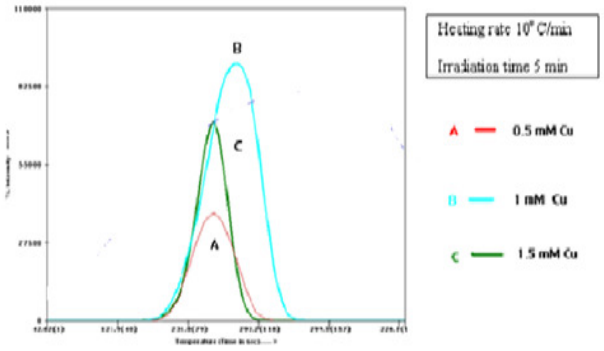

Fig 3. TL glow curves for ZnS:Cu with different concentrations of Cu (10gm SHMP).

The change of TL is consistent with that of the surface fluorescence. It is reasonable to consider that the TL of the nanoparticles is correlated to the surface state. The glow peaks in Fig. 3 are caused by the trapped carriers which are produced during the sample processing. As the particles become smaller, ions at the surface increase rapidly. In nanoparticles, most ions at the surface are not saturated in coordination, electrons or holes may be excited easily and escape from the ions, and then they are trapped at surface states located in the forbidden gap. When the sample is heated the detrapping of electrons and their subsequent recombination with holes gives rise to the light emission [22].

CONCLUSIONS

Quantum dots of coper doped zinc sulphide have been successfully synthesized by a chemical precipitation reaction method. It was observed that the particle sizes are dependant on the amounts of stabilizing agents (SHMP) used during synthesis making it possible to alter the particle sizes by changing the weight of stabilizing agents. ZnS: Cu has zinc blende structure, as observed by X-ray diffraction, and has a crystallite size of 2nm to 3nm as calculated by Debye-Scherer formula. The TL properties of ZnS doped with copper nanophosphors have been investigated for UV irradiation. The optimum concentration of Cu is 1mM. After that the TL intensity decreases with increasing concentration of Cu. The trapping parameters were calculated by initial rise method and half width method. From both the method activation energy and trap depth lies between 0.78eV to 2.43eV and frequency factor lies between $0.16*10^{8}$ to $4.09*10^{11}$. From the absorption spectra of SHMP capped ZnS: Cu has observed that the absorption edge increases from 230 to 250nm with a change in weight of SHMP capping agent from 2gm to 10gm. The blue shift in the absorption edge is a measure of increasing band gap that can be attributed to the presence of smaller crystallites due to quantum confinement effects.

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